## REVERSE OSMOSIS: APPLICATION TO POTATO-STARCH FACTORY WASTE EFFLUENTS

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One of the major problems of our country, and most others, is pollution of the water supplies. In this paper, we hope to describe for you a specific pollution problem of great importance, a possible means of alleviating this problem, and a possible role of reverse osmosis in the technology under consideration.

Since all of you are well versed in most aspects of reverse osmosis, little time need be spent on background material for this phase. It is assumed, however, that few of you are familiar with the problems of pollution and waste treatment faced by the food industry in general and the potato-starch industry in particular. Therefore, to make it easier later, a little background material will be presented. Only problems concerning the potato-starch industry will be discussed.

In the manufacture of potato starch, the tubers are removed from storage by means of flowing-water flumes, which transport them to a conveyer and at the same time remove vegetative parts, soil, and stones. This water is usually sent to settling ponds prior to recycling to the flumes and thus does not enter into the immediate problem. After washing, the tubers are ground or rasped to a slurry. This slurry is screened and washed by various means with large quantities of water to separate the starch from the fibrous material, and, finally, the starch is centrifuged and again washed with copious quantities of water to remove all remaining soluble materials. On the average, the solids content of potatoes is 19 percent (Table 1). The starch content runs about 13 percent on a fresh-weight basis. This means that about 6 percent of the fresh weight consists of nonstarch solids, and these end up in the waste effluent. Until about 10 years ago, disposal of this waste material consisted simply of its being dumped into the nearest river. Esthetic and survival considerations, however, have made it necessary to end pollution of this nature, and Federal and state laws have been enacted which require treatment of the effluent before returning the water to the river.

Considering an average starch plant producing 30 tons of starch per day, about 14 tons of nonstarch solids end up in the waste effluent from the factory. This waste contains both insoluble materials, termed primary waste, and soluble materials, termed secondary waste. The

TABLE 1. AVERAGE COMPOSITION OF POTATOES PROCESSED IN MAINE STARCH FACTORIES(a)

Substance	Percent
Starch	13
Protein (N x 6.25)	2
Cellulosic material	1.5
Sugars	0.5
Minerals (ash)	1
Miscellaneous minor constituents (total)	1
Water	81

<sup>(</sup>a) From Potato Processing, Talburt and Smith, AVI Pub. Co., p 451 (1967).

starch industry has developed settling, screening, centrifuging, and filtering procedures designed to remove the primary waste; to date, disposal of this product has consisted of selling it as a cattle feed. Therefore, it does not loom as an immediate pollution problem.

The secondary waste is another story. This material contains protein, free amino acids, organic acids, sugars, inorganic ions, and other compounds in minor concentrations. The output of this waste from a 30-ton-per-day starch plant is about 300 gpm or about 432,000 gallons per day. The solids content is about 0.5 to 1.0 percent, and it has a chemical-oxidation-demand (COD) requirement of approximately 9000-14000 mg per liter. This is equivalent to a city of approximately 85,000 people, with respect to waste-disposal potential. Presently, it is pumped into lagoons, where biological action removes the dissolved organic solids. Lagooning is a relatively inefficient process and, since the potato solids are quite resistant to treatment, it is necessary to employ large land areas for the treatment process. Even with this treatment, only about 80 percent of the COD requirement can be removed. In addition, the odor emanating from many treatment ponds is most unpleasant, to say the least. In the near future, it is quite possible that the law will require treatment of such waste to the extent that the renovated water returned to the river will be no different than the water that was removed up river for use in processing. It has been estimated that the facilities required to produce this quality of water effluent would cost 80 percent or more of the present plant investment. Since starch factories are marginal enterprises, they could not afford such expenditures and would have to go out of business, thus causing a shortage of this important item and also loss of an outlet for cull potatoes that is very important to the potato industry. Since potato starch is a valued product in many applications with the industry volume at approximately \$10,000,000 per year based upon the selling price, this would be a serious loss.

The present methods of renovation do not bring any monetary return on the secondary-waste-treatment investment. Improving this situation may be the means for solution of the dilemma. Any treatment procedure that includes processes yielding a monetary return would ease and distribute the cost. Such return could mean the difference between failure and continued business for a marginal company.

The proteins and amino acids have been shown to contain more than adequate amounts of lysine and methionine for human and animal nutrition<sup>(1)</sup> and, as such, would have considerable value on the market as additives to certain grain products and as starting materials

for new food products or flavoring agents. The Dutch have developed a process for recovering proteins (2), and the USDA has published on means of recovery of the free amino acids by ion exchange (3,4) The inorganic ions must be removed prior to the ion-exchange removal of free amino acids (5), and they have value as a fertilizer because of their high potassium content. The organic acids have value due to their high citric-acid content. (6) A project aimed at recovery of these products has been initiated. By removing these organic compounds, the COD requirement of the remaining effluent would be decreased to 20-25 percent of that of the original waste. Also, the organic acid recovery step removes 98 percent of the phosphorus, which would help to eliminate algae growth in the final lagoon treatment where the remaining organic matter, mostly sugars, would be biologically treated. The income from the sale of these products would probably pay a major portion of the cost of treatment.

At a solids concentration of 0.5 percent, the efficiency of recovery of protein by heat and acid coagulation and the removal of amino acids, inorganic ions, and organic acids by ion-exchange procedures is relatively low. At a solids concentration of 2-4 percent, these processes have been shown to be quite efficient. (5) The usual concentration methods, such as distillation and freezing, are expensive to use, especially when such large volumes are involved. Therefore, studies are in progress on the use of reverse osmosis for application to these problems because the actual expense of operation is low. This latter statement will be discussed more fully subsequently.

For several reasons, the Havens "Osmotik Processor" was chosen for this work (Figure 1). This apparatus is portable and has an input capacity of about 3 gpm, which is a good size for development work in which limited supplies of the solution to be concentrated are available. In addition, the modules are made up of 1/2-inch-diameter tubes and serve this purpose extremely well because the starch-waste influent usually contains some finely divided, insoluble solids. These solids tend to settle on a flat membrane or to plug up a module made in rolls or disks with narrow spacers. The tube type can be easily opened and flushed with water or scoured by the use of a 1/2-inch-diameter polyfoam plug followed by water. Sterilization of the apparatus with hypochlorite is facilitated by the geometry of the module.

The apparatus, as purchased, had 24 modules of seven tubes each. Eight modules contained the coarse-porosity membrane, eight contained the membrane of intermediate porosity, and eight contained the fine membrane. They can be operated individually, in parallel, or in series. Each unit of eight modules contains 52 square feet of membrane. Due to a limited supply of waste effluent, much of the early work was performed by returning the concentrate to the supply. This, of course, produced an ever increasing concentration of effluent.

Most of the work to be discussed was done on a simulated waste effluent produced by grinding potatoes, filtering, and washing to give a concentrated product (in a manner similar to that employed in a starch factory) which was diluted to the desired solids content before use in a particular experiment.

Due to the limited time available, a few typical examples of experiments have been chosen which indicate the possibilities of the procedure. A preliminary run, using all modules in series (coarse, intermediate, and fine, in that order), an input of 50 gallons of the simulated

<sup>\*</sup>Mention of company or trade names does not imply endorsement by the Department over others not named.

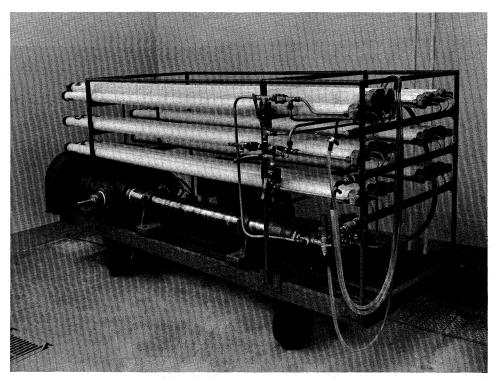


Figure 1. Experimental reverse-osmosis equipment.

waste effluent containing 0.32 percent solids, a pressure of 600 psi, and recirculation of the concentrate, produced in a period of 45 minutes the results shown in Table 2.

This short experiment showed that the waste effluent could be concentrated by reverse osmosis. However, little, if any, information was obtained for individual membrane types as to flux, comparison of membrane properties, solids in the permeate, etc.

Using a concentrating system in which the permeate was removed and the concentrate was returned to the feed tank to be recirculated, experiments were run by pumping a measured volume of waste water through the coarse-membrane modules only, the intermediate-membrane modules only, and the fine-porosity membranes only. All permeate was collected and, at the end of each run, all the concentrate was collected. Using this method, a reasonable measure of all volumes including initial feed, permeate, and concentrate, was obtained. Analyses of these three fractions gave a measure of the performance of each system with respect to retention of the waste-water constituents in which we are interested.

In a typical experiment, about 55 gallons of the waste water, at 0.5 percent solids concentration, was charged to a feed tank. This was pumped through the medium or intermediate-porosity-membrane modules with the concentrate being recirculated. All permeate was collected. The operating pressure was 600 psi and the pumping rate was 3 gpm. When 41 gallons of permeate had been collected (about 75 percent removal of water), the run was

TABLE 2. CONCENTRATION OF WATER USING VARIOUS REVERSE-OSMOSIS MODULES IN SERIES

		garan kan di s	Permeate	
Elapsed Time, min	Membranes Used	Concentrate Solids, ppm(a)	Solids, ppm	Conductivity, ppm Cl
10	All	4790	87	
13	Coarse	5050	148	80
22	All	6090	99	
29	Fine	6680	25	10
30	Intermediate	<b></b> * √	39	20
35	All	8400	110	
39	All	9700	137	
45 (end)		9620 (0.96%)(b)		

<sup>(</sup>a) Concentrate sample taken when concentrate left apparatus but before mixing with remaining concentrate to be recycled.

stopped. All of the final concentrate was collected. The total solids of 1.9 percent indicated a fourfold concentration At the start of the run, the flux was 10.2 gf<sup>2</sup>d at 77 F. At the end, the flux was 8.8 gf<sup>2</sup>d at 95 F. The pH of the concentrate changed from 6.4 to 6.7. A summary of the data is shown in Table 3.

After completing the tests on all three membranes, the following conclusions could be drawn:

- (1) Analysis of the permeates from all three membranes showed that the recovered water was pure enough for reuse in a plant. The medium-porosity membrane did a much better job of retaining the desirable constituents than did the coarse one. Solids retention was not greatly improved by the use of the fine membrane.
- (2) The average fluxes for the membranes were 11.5  $gf^2d$  for the coarse, 9.5  $gf^2d$  for the medium, and 7.8  $gf^2d$  for the fine.
- (3) A fourfold increase in total solids of the concentrate increased the COD by roughly fourfold in all three cases. The COD of the three permeates, however, showed considerable difference. The COD of the coarse-membrane permeate equalled 268 ppm or a reduction of about 94 percent. That of the medium membrane was equivalent of a 98 percent reduction and that of the fine at 40 ppm equalled a 99 percent reduction.

These results indicated that the best choice of the three types of membranes tested was the one of medium porosity. This conclusion was based upon the relationships between flux, retention of desirable waste-water constituents, and reduction of COD.

Most of the membrane designs described in the literature are aimed at increasing the efficiency of production of pure product water rather than the concentrate. Several attempts to increase the rate of concentration, with final automation in mind, have been made. Preliminary experimentation has shown it quite possible to modify the equipment so that a concentrate

<sup>(</sup>b) Final solids in concentrate measured after thorough mixing of entire concentrate.

TABLE 3. COD OF WASTE WATER ON CONCENTRATION BY REVERSE OSMOSIS

Feed	Total Solids, percent	COD, ppm
Coarse membrane	0.43	3,670
Medium membrane	0.49	4,269
Fine membrane	0.43	3,838
		And the second s
Concentrate		
Coarse membrane	1.60	13,364
Medium membrane	1.93	16,163
Fine membrane	1.57	13,784
Permeate		
Coarse membrane	0.035	268
Medium membrane	0.012	91
Fine membrane	0.005	40

containing a constant-specific solids concentration can be produced. The concentrate is returned to the RO unit by-passing the feed tank. As permeate is taken off, an equal volume of fresh feed is introduced. When the desired equilibrium concentration is reached, concentrate is also drawn off at a constant rate and replaced with fresh feed as required to keep up the flow rate. Figure 2 roughly shows the pathways employed in the batchwise configuration and in the continuous configuration. Table 4 shows an example of the continuous results obtained. Table 5 shows the data obtained when the batchwise system was used.

Comparing the times of operation, the flux, and the concentrations obtained, it is apparent, under the operating conditions employed, that the batchwise operation is more efficient. With use of conductivity measurements to follow the concentration by the batchwise procedure, switching from one feed tank to a new one would be quite simple. These data also indicate that other ways for increasing the efficiency should be investigated and experiments are now under way to study parallel and series operation as well as combinations of these to determine the best approach.

These experiments also show the importance of changes in flux as an experiment progresses and as a membrane is subjected to extended use. It is apparent that the flux decreased over the period of time required to carry out the studies reported. No attempt has been made to determine how permanent these changes may be, but such studies are planned for the near future.

Current work, in progress, involves a variation of the type of treatment just discussed. A new membrane is available having a porosity such that the amino acids, organic acids, sugars,

TABLE 4. CONTINUOUS OPERATION OF REVERSE-OSMOSIS EQUIPMENT(a)

Elapsed Time, min	Takeoff	Flux <sup>(b)</sup> , gf <sup>2</sup> d	Total Solids, concentrate percent	Permeate Conductance, mhos
0	Permeate	9.4	. Orangan	
15	"	8.8		2.16 x 10 <sup>-4</sup>
60	" '	6.7		3.70
90	"	5.9		4.44
120	"	5.3		5.14
150	<i>n</i>	4.9	<del></del>	5.43
	Со	ncentrate Taked	off Started	
160	<b>n</b>	4.7	3.8	5.38 x 10 <sup>-4</sup>
190	"	4.7	3.2	4.45
220	n e	4.4	2.8	4.25
250	"	3.8	2.4	3.89
310	"	4.2	2.2	3.77
370	"	4.0	2.3	4.19

Total waste treated = 85 gal at 0.5 percent
Total concentrate = 15 gal at 2.7 percent
Total permeate = 70 gal

<sup>(</sup>b) Pressure = 600 psi.

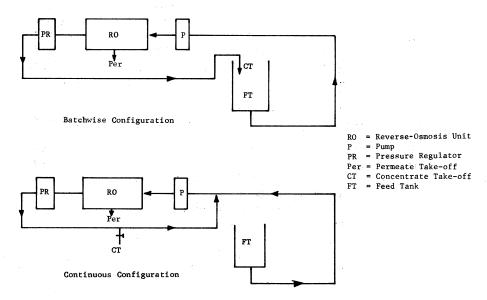


Figure 2. Illustration of batchwise and continuous configurations employed in efficiency experiments.

<sup>(</sup>a) Medium-porosity membrane used. Area = 52 sq ft.

TABLE 5. BATCHWISE OPERATION OF REVERSE-OSMOSIS EQUIPMENT(a)

Elapsed Time, min	Takeoff	Flux <sup>(b)</sup> , gf <sup>2</sup> d	Total Solids, concentrate percent	Conductance, mhos
	Concentrate		0.50	
0	Permeate	9.8	<b>0.00</b>	
	Concentrate		0.55	1.50 x 10 <sup>-3</sup>
18	Permeate	9.2	0.00	1.14 x 10 <sup>-4</sup>
	Concentrate		0.58	1.85 x 10 <sup>-3</sup>
38	Permeate	8.5		1.37 × 10 <sup>-4</sup>
	Concentrate		0.67	2.08 x 10 <sup>-3</sup>
58	Permeate	8.1		1.41 × 10 <sup>-4</sup>
	Concentrate		0.75	2.23 x 10 <sup>-3</sup>
78	Permeate	7.4		1.54 x 10 <sup>-4</sup>
	Concentrate		0.91	2.78 x 10-3
98	Permeate	6.8		1.64 × 10 <sup>-4</sup>
	Concentrate		1.09	3.35 x 10-3
118	Permeate	6.7	1.00	1.96 x 10 <sup>-4</sup>
	Concentrate		1.29	4.15 x 10-3
138	Permeate	6.4	1.29	2.51 x 10 <sup>-4</sup>
	Concentrate		1.62	5.13 x 10 <sup>-3</sup>
158	Permeate	6.0		3.54 x 10 <sup>-4</sup>
	Concentrate		3.36	9.87 x 10 <sup>-3</sup>
168	Permeate	5.1		5.09 x 10 <sup>-4</sup>

Total waste treated = 55 gal at 0.5 percent
Total concentrate = 6 gal at 3.6 percent
Total permeate = 47 gal

<sup>(</sup>a) Medium-porosity membrane. Area = 52 sq ft.

<sup>(</sup>b) Pressure = 600 psi.

and inorganic ions pass through in the permeate and the protein remains in the concentrate. Preliminary trials with this membrane indicate that a multiple-stage concentration could be employed. One of the questions that immediately came up was the sequence of use of the two types of membranes. Figure 3 shows two possible configurations. Each has certain theoretical advantages and disadvantages that must be studied. In the first system, the permeate from the very coarse membrane would contain the soluble, low-molecular-weight materials and the concentrate would contain the protein. The permeate then would pass through the intermediate membrane, producing pure water in the permeate, and the concentrate would contain only the low-molecular-weight solubles. In the second system, the effluent would be passed through the intermediate-porosity membrane to produce pure water as the permeate, and the concentrate, containing all soluble materials from the waste, would be sent through the new, very coarse membrane. The amino acids, organic acids, sugars, and inorganic ions would be in the permeate and the proteins would be in the concentrate.

The first method would pass the entire effluent through the membrane with the highest flux, allowing a smaller quantity to pass through the more dense membrane. Whether the increased concentration of this concentrate would have such a high osmotic pressure as to cause trouble in the finer membrane is not yet answered. The second method may be slower, but the increase in osmotic pressure would not be as important. In either case, the supernatant liquid from the protein precipitation would probably have to be returned to the

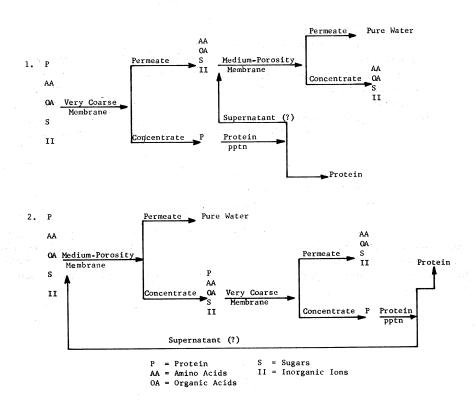


Figure 3. Variations in reverse-osmosis treatments of waste water.

intermediate-porosity-membrane cycle, because the amount of solubles not precipitated by heat and acid coagulation of the protein could be too high to be returned directly to waste or be reused in the plant. The concentration of the desirable constituents obtained by each method will have to be studied, and this may play an important part in the final selection of the method. The fact that the protein can be separated from the other constituents being isolated is important, because the rate of operation of the ion-exchange section would not be dependent on the rate of removal of protein.

This experimental work is either in progress or planned for the near future. Not enough data are available to give direct answers to all of the practical and theoretical questions. However, the final use of the procedure in a plant will be based upon the relative efficiencies of the different possible configurations as well as how they adapt to the recovery processes for which concentration is necessary. The questions, though, serve to point out and demonstrate the problems involved and the types of investigations that must be carried out in practicalapplication work of this type. It is believed that these and other experiments discussed herein show that the concentration of potato-starch-factory secondary waste can be carried out by reverse osmosis and that actual operating costs would be favorable. As yet, membrane life under these and factory conditions has not been determined. However, we must be practical in any application such as this. At a flux of even as high as 9.5 gf<sup>2</sup>d for the intermediate-porosity membrane, treatment of 432,000 gallons per day of waste effluent to produce a fourfold increase in concentration would require the use of 2043 modules (18 tubes each) which, at the current price of \$150 each, would cost \$306,450 just for the membranes alone. This does not consider replacement of modules due to possible malfunction or the life expectancy being exceeded. Also, no real estimate of what the remainder of a plant, such as pumps, valves, piping, measuring devices, etc., would require is available at this time; but it is safe to say that, with this additional cost, the processing system would not be considered seriously by the industry. We believe the process to have merit and, if the cost of modules can be brought down to a more reasonable figure, it would be employed by the starch industry. There is also a great possibility that the potato-processing industry, made up of manufacturers of flakes, granules, dice, chips, French fries, etc., would also be open to its use, especially for in-plant treatment of waste for immediate reuse of water.

Another phase of the work which will require attention is the sterility problem. As you know, this is a major problem of any food or drug processing industry. As feasibility studies are completed, it will be necessary to demonstrate adequate biological control.

It is hoped that this discussion has shown the type of work required in any practical-application study of reverse osmosis. Since the original cost and replacement cost of membranes is so important to acceptance of the technique by the potato-starch industry, it is also hoped that this paper will help in promoting accelerated studies on membrane production aimed at decreasing these costs.

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